



## V1.42In1.83Mo15Se19

Patrick Gougeon, Philippe Gall, Salloum Diala, Potel Michel

### ► To cite this version:

Patrick Gougeon, Philippe Gall, Salloum Diala, Potel Michel. V1.42In1.83Mo15Se19. Acta Crystallographica Section E: Structure Reports Online [2001-2014], 2010, 66 (10), pp.i73. 10.1107/S1600536810036834 . hal-00538234

**HAL Id: hal-00538234**

**<https://hal.science/hal-00538234>**

Submitted on 9 Jul 2013

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# $V_{1.42}In_{1.83}Mo_{15}Se_{19}$

Patrick Gougeon,\* Philippe Gall, Diala Salloum and Michel Potel

Sciences Chimiques de Rennes, UMR CNRS No. 6226, Université de Rennes I – INSA Rennes, Avenue du Général Leclerc, 35042 Rennes CEDEX, France  
Correspondence e-mail: Patrick.Gougeon@univ-rennes1.fr

Received 6 September 2010; accepted 14 September 2010

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(Mo-Se) = 0.001$  Å; disorder in main residue;  $R$  factor = 0.037;  $wR$  factor = 0.087; data-to-parameter ratio = 35.7.

The structure of the title compound, vanadium indium pentadecamolybdenum nonadecaselenide,  $V_{1.42}In_{1.83}Mo_{15}Se_{19}$ , is isotypic with  $In_{2.9}Mo_{15}Se_{19}$  [Grüttner *et al.* (1979). *Acta Cryst. B* **35**, 285–292]. It is characterized by two cluster units  $Mo_6Se_8Se_6^i$  and  $Mo_9Se_{11}Se_6^a$  (where  $i$  represents inner and  $a$  apical atoms) that are present in a 1:1 ratio. The cluster units are centered at Wyckoff positions  $2b$  and  $2c$  and have point-group symmetry  $\bar{3}$  and  $\bar{6}$ , respectively. The clusters are interconnected through additional Mo–Se bonds. In the title compound, the  $V^{3+}$  cations replace the trivalent indium atoms present in  $In_{2.9}Mo_{15}Se_{19}$ , and a deficiency is observed on the monovalent indium site. One Mo, one Se and the V atom are situated on mirror planes, and two other Se atoms and the In atom are situated on threefold rotation axes.

## Related literature

For previous reports on the crystal structure of  $In_{\sim 3}Mo_{15}Se_{19}$  compounds, see: Grüttner *et al.* (1979). For physical properties of this type of compound, see: Seeber *et al.* (1979). The crystal structures of the substituted compounds  $Ho_{0.76}In_{1.68}Mo_{15}Se_{19}$  and  $In_{0.87}K_2Mo_{15}Se_{19}$  were reported by Salloum *et al.* (2006; 2007). For details of the  $i$ - and  $a$ -type ligand notation, see: Schäfer & von Schnering (1964).

## Experimental

### Crystal data

$V_{1.42}In_{1.83}Mo_{15}Se_{19}$   
 $M_r = 3221.80$   
Hexagonal,  $P6_3/m$   
 $a = 9.7361$  (1) Å  
 $c = 19.3090$  (4) Å  
 $V = 1585.11$  (4) Å<sup>3</sup>

$Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 29.21$  mm<sup>−1</sup>  
 $T = 293$  K  
 $0.09 \times 0.07 \times 0.05$  mm

### Data collection

Nonius KappaCCD diffractometer  
Absorption correction: analytical  
(de Meulenaar & Tompa, 1965)  
 $T_{min} = 0.161$ ,  $T_{max} = 0.329$

27560 measured reflections  
2390 independent reflections  
1634 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.093$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.087$   
 $S = 1.08$   
2390 reflections

67 parameters  
 $\Delta\rho_{max} = 3.22$  e Å<sup>−3</sup>  
 $\Delta\rho_{min} = -2.57$  e Å<sup>−3</sup>

Table 1

Selected bond lengths (Å).

Mo2–Se5	2.5259 (8)	Mo3–Se2	2.5631 (6)
Mo2–Se2	2.5974 (6)	Mo3–Se2 <sup>vii</sup>	2.5631 (6)
Mo2–Se2 <sup>i</sup>	2.6290 (6)	Mo3–Se3	2.5965 (9)
Mo2–Mo2 <sup>i</sup>	2.6474 (7)	Mo3–Se3 <sup>i</sup>	2.6095 (9)
Mo2–Se1 <sup>ii</sup>	2.6504 (6)	Mo3–Mo3 <sup>viii</sup>	2.7056 (10)
Mo2–Se3 <sup>i</sup>	2.6966 (6)	Mo3–Mo2 <sup>ix</sup>	2.7136 (5)
Mo2–Mo3 <sup>i</sup>	2.7136 (5)	In1–Se5	3.0759 (15)
Mo2–Mo3	2.7557 (5)	In1–Se2 <sup>x</sup>	3.1221 (5)
Mo1–Se1 <sup>iii</sup>	2.5467 (7)	In1–Se1 <sup>x</sup>	3.4904 (7)
Mo1–Se4	2.5481 (8)	V1–Se4	2.510 (2)
Mo1–Se1	2.5717 (6)	V1–Se3 <sup>iv</sup>	2.730 (3)
Mo1–Se1 <sup>iv</sup>	2.6111 (6)	V1–Se2 <sup>v</sup>	2.7981 (18)
Mo1–Se2	2.6378 (7)	V1–Se3 <sup>v</sup>	2.831 (3)
Mo1–Mo1 <sup>v</sup>	2.6992 (7)	V1–Mo3 <sup>v</sup>	2.865 (3)
Mo1–Mo1 <sup>vi</sup>	2.7223 (8)		

Symmetry codes: (i)  $-y + 1, x - y, z$ ; (ii)  $-x + y + 1, -x, z$ ; (iii)  $x - y, x, -z + 1$ ; (iv)  $-y, x - y, z$ ; (v)  $-x + y, -x, z$ ; (vi)  $y, -x + y, -z + 1$ ; (vii)  $x, y, -z + \frac{3}{2}$ ; (viii)  $-x + y + 1, -x + 1, z$ ; (ix)  $-x + y + 1, -x + 1, -z + \frac{3}{2}$ ; (x)  $-x + 1, -y, -z + 1$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2403).

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bergerhoff, G. (1996). *DIAMOND*. University of Bonn, Germany.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Grüttner, A., Yvon, K., Chevrel, R., Potel, M., Sergent, M. & Seeber, B. (1979). *Acta Cryst. B* **35**, 285–292.
- Meulenaar, J. de & Tompa, H. (1965). *Acta Cryst. A* **19**, 1014–1018.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Salloum, D., Gougeon, P. & Potel, M. (2006). *Acta Cryst. E* **62**, i83–i85.
- Salloum, D., Gougeon, P. & Potel, M. (2007). *Acta Cryst. E* **63**, i8–i10.
- Schäfer, H. & von Schnering, H. G. (1964). *Angew. Chem.* **76**, 833–845.
- Seeber, B., Decroux, M., Fisher, Ø., Chevrel, R., Sergent, M. & Grüttner, A. (1979). *Solid State Commun.* **29**, 419–423.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

**supplementary materials**

*Acta Cryst.* (2010). E66, i73 [ doi:10.1107/S1600536810036834 ]

## V<sub>1.42</sub>In<sub>1.83</sub>Mo<sub>15</sub>Se<sub>19</sub>

P. Gougeon, P. Gall, D. Salloum and M. Potel

### Comment

From the point of view of crystal chemistry and physical properties, the reduced molybdenum selenides In<sub>3</sub>Mo<sub>15</sub>Se<sub>19</sub> (Grüttner *et al.*, 1979) constitute an interesting family of compounds. Indeed, their crystal structure contains an equal mixture of Mo<sub>6</sub> and Mo<sub>9</sub> cluster units and the In atoms occupy two crystallographically different positions depending on their formal oxidation state of +1 or +3. Recently, we have shown that the In<sup>3+</sup> cation can be replaced by other trivalent cations such as Ho<sup>3+</sup> (Salloum *et al.*, 2006) and the In<sup>+</sup> cation by K<sup>+</sup> (Salloum *et al.*, 2007). Interest in these Mo cluster compounds also lies in their physical properties, because they become superconductors with high critical magnetic fields at about 4 K (Seeber *et al.*, 1979). We present here the crystal structure of V<sub>1.42</sub>In<sub>1.83</sub>Mo<sub>15</sub>Se<sub>19</sub> in which a 3d element replaces the trivalent indium atom.

The Mo—Se framework of the title compound consists of the cluster units Mo<sub>6</sub>Se<sup>*i*</sup><sub>8</sub>Se<sup>*a*</sup><sub>6</sub> and Mo<sub>9</sub>Se<sup>*i*</sup><sub>11</sub>Se<sup>*a*</sup><sub>6</sub> in a 1:1 ratio (for details of the *i*- and *a*-type ligand notation, see: Schäfer & von Schnering (1964)). Both cluster units are interconnected through additional Mo—Se bonds (Figs. 1 and 2). The first unit can be described as an Mo<sub>6</sub> octahedron surrounded by eight face-capping inner Se<sup>*i*</sup> and six apical Se<sup>*a*</sup> ligands. The Mo<sub>9</sub> cluster is surrounded by 11 Se<sup>*i*</sup> atoms capping one or two faces of the biocuboctahedron and six Se<sup>*a*</sup> ligands above the apical Mo atoms. The Mo<sub>6</sub>Se<sup>*i*</sup><sub>8</sub>Se<sup>*a*</sup><sub>6</sub> and Mo<sub>9</sub>Se<sup>*i*</sup><sub>11</sub>Se<sup>*a*</sup><sub>6</sub> units are centered at Wyckoff positions 2*b* and 2*c* and have point-group symmetry  $\bar{3}$  and  $\bar{6}$ , respectively. The Mo—Mo distances within the Mo<sub>6</sub> cluster are 2.6992 (7) Å for the distances of the Mo triangles formed by the Mo1 atoms related through the threefold axis, and 2.7223 (8) Å for the distances between these triangles. The Mo—Mo distances within the Mo<sub>9</sub> clusters are 2.6474 (7) and 2.7056 (10) Å in the triangles formed by the atoms Mo2 and Mo3, respectively, and 2.7136 (5) and 2.7557 (5) Å for those between the Mo2<sub>3</sub> and Mo3<sub>3</sub> triangles. The Se atoms bridge either one (Se1, Se2, Se4 and Se5) or two (Se3) triangular faces of the Mo clusters. Moreover, atoms Se1 and Se2 are linked to an Mo atom of a neighboring cluster. The Mo—Se bond lengths range from 2.5467 (7) to 2.6378 (7) Å within the Mo<sub>6</sub>Se<sup>*i*</sup><sub>8</sub>Se<sup>*a*</sup><sub>6</sub> unit, and from 2.5259 (8) to 2.6966 (6) Å within the Mo<sub>9</sub>Se<sup>*i*</sup><sub>11</sub>Se<sup>*a*</sup><sub>6</sub> unit. Each Mo<sub>9</sub>Se<sup>*i*</sup><sub>11</sub>Se<sup>*a*</sup><sub>6</sub> cluster is interconnected by six Mo<sub>6</sub>Se<sup>*i*</sup><sub>8</sub>Se<sup>*a*</sup><sub>6</sub> units (and vice versa) via Mo2—Se1 bonds (and Mo1—Se2 bonds, respectively), forming the three-dimensional Mo—Se framework, the connectivity formula of which is Mo<sub>9</sub>Se<sup>*i*</sup><sub>5</sub>Se<sup>*i-a*</sup><sub>6/2</sub>Se<sup>*-ai*</sup><sub>6/2</sub>, Mo<sub>6</sub>Se<sup>*i*</sup><sub>2</sub>Se<sup>*i-a*</sup><sub>6/2</sub>Se<sup>*-i*</sup><sub>6/2</sub>. It results from this arrangement that the shortest intercluster Mo1—Mo2 distance is 3.4216 (6) Å, indicating only weak metal—metal interaction. The In<sup>+</sup> cations are surrounded by seven Se atoms forming a distorted tricapped tetrahedron, as is the case in In<sub>2.9</sub>Mo<sub>15</sub>Se<sub>19</sub>. The Se5 and Se2 atoms forming the tetrahedron are at 3.0759 (15) and 3.1221 (5) Å from the In atom, and the capping Se1 atoms are at 3.4904 (7) Å. The V<sup>3+</sup> cations, as the In<sup>3+</sup> cations in the In<sub>3</sub>Mo<sub>15</sub>Se<sub>19</sub> compounds, occupy partially at 47.4 (6)% a triangular group of distorted octahedral cavities, which are formed by two Mo<sub>6</sub>Se<sup>*i*</sup><sub>8</sub>Se<sup>*a*</sup><sub>6</sub> and three Mo<sub>9</sub>Se<sup>*i*</sup><sub>11</sub>Se<sup>*a*</sup><sub>6</sub> units, around the threefold rotation axis. The V—Se distances are in the 2.510 (2) - 2.831 (3) Å range.

## Experimental

Single crystals of  $V_{1.42}In_{1.83}Mo_{15}Se_{19}$  were prepared from a mixture of  $V_2Se_3$ ,  $MoSe_2$ ,  $InSe$  and  $Mo$  with a nominal composition  $V_{1.5}In_2Mo_{15}Se_{19}$ . Before use,  $Mo$  powder was reduced under  $H_2$  flowing gas at 1273 K during ten hours in order to eliminate any trace of oxygen. The binaries  $V_2Se_3$ ,  $MoSe_2$ ,  $InSe$  were obtained by heating stoichiometric mixtures of the elements in sealed evacuated silica tubes during about 2 days. All handlings of materials were done in an argon-filled glove box. The initial mixture (*ca.* 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low argon pressure using an arc welding system. The charge was heated at the rate of 300 K/h up to 1773 K, the temperature which was held for 48 hours, then cooled at 100 K/h down to 1373 K and finally furnace cooled.

## Refinement

The highest peak and the deepest hole are located 1.56 Å and 0.66 Å from  $Mo_3$ , respectively. Refinement of the occupancy factors of the V and In atoms led to the final composition  $V_{1.42(2)}In_{1.832(8)}Mo_{15}Se_{19}$ .

## Figures

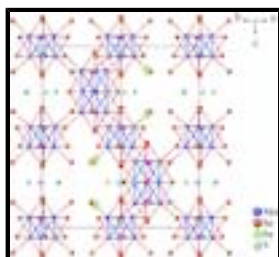


Fig. 1. View of  $V_{1.42}In_{1.83}Mo_{15}Se_{19}$  along [110]. Displacement ellipsoids are drawn at the 97% probability level.

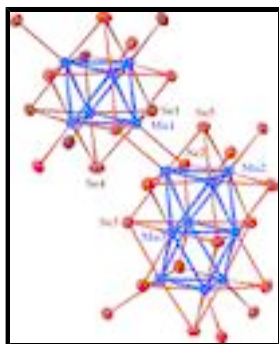


Fig. 2. Plot showing the atom-numbering scheme and the interunit linkage of the  $Mo_9Se_{11}Se_6$  and  $Mo_6Se_8Se_6$  cluster units. Displacement ellipsoids are drawn at the 97% probability level.

## vanadium indium pentadecamolybdenum nonadecaselenide

### Crystal data

$V_{1.42}In_{1.83}Mo_{15}Se_{19}$

$M_r = 3221.80$

Hexagonal,  $P6_3/m$

Hall symbol:  $-P\ 6c$

$a = 9.7361(1)\text{ Å}$

$c = 19.3090(4)\text{ Å}$

$D_x = 6.750\text{ Mg m}^{-3}$

$Mo\ K\alpha$  radiation,  $\lambda = 0.71069\text{ Å}$

Cell parameters from 26495 reflections

$\theta = 2.6\text{--}35.0^\circ$

$\mu = 29.21\text{ mm}^{-1}$

$T = 293\text{ K}$

$V = 1585.11 (4) \text{ \AA}^3$   
 $Z = 2$   
 $F(000) = 2797$

Irregular block, black  
 $0.09 \times 0.07 \times 0.05 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
Radiation source: fine-focus sealed tube  
graphite  
 $\varphi$  scans ( $\kappa = 0$ ) + additional  $\omega$  scans  
Absorption correction: analytical (de Meulenaar & Tompa, 1965)  
 $T_{\min} = 0.161$ ,  $T_{\max} = 0.329$   
27560 measured reflections

2390 independent reflections  
1634 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.093$   
 $\theta_{\max} = 35.0^\circ$ ,  $\theta_{\min} = 2.6^\circ$   
 $h = -15 \rightarrow 15$   
 $k = -15 \rightarrow 12$   
 $l = -30 \rightarrow 31$

### Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.087$   
 $S = 1.08$   
2390 reflections  
67 parameters  
0 restraints

Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map  
 $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.9587P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 3.22 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -2.57 \text{ e \AA}^{-3}$   
Extinction correction: *SHELXL97* (Sheldrick, 2008),  
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.00025 (5)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mo1	0.16776 (5)	0.01669 (5)	0.55780 (2)	0.00914 (10)	
Mo2	0.68407 (5)	0.18577 (5)	0.63317 (2)	0.00965 (10)	
Mo3	0.51292 (7)	0.16694 (7)	0.7500	0.00868 (11)	

## supplementary materials

Se1	0.03647 (6)	−0.28702 (6)	0.55134 (3)	0.01070 (11)	
Se2	0.37798 (6)	0.00665 (6)	0.64065 (3)	0.01233 (12)	
Se3	0.34594 (8)	0.30753 (9)	0.7500	0.01280 (15)	
Se4	0.0000	0.0000	0.66221 (5)	0.01643 (19)	
Se5	0.6667	0.3333	0.52902 (5)	0.01225 (17)	
In1	0.6667	0.3333	0.36972 (6)	0.0374 (4)	0.916 (4)
V1	−0.2026 (4)	−0.1744 (3)	0.7500	0.0177 (9)	0.474 (6)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mo1	0.00996 (18)	0.00853 (18)	0.0089 (2)	0.00456 (15)	0.00070 (14)	−0.00012 (14)
Mo2	0.00995 (18)	0.00993 (18)	0.0089 (2)	0.00488 (15)	0.00013 (14)	−0.00037 (14)
Mo3	0.0096 (2)	0.0099 (3)	0.0071 (3)	0.0053 (2)	0.000	0.000
Se1	0.0110 (2)	0.0097 (2)	0.0116 (2)	0.00543 (19)	0.00107 (17)	0.00229 (17)
Se2	0.0115 (2)	0.0119 (2)	0.0138 (3)	0.00598 (18)	−0.00305 (18)	−0.00208 (18)
Se3	0.0121 (3)	0.0158 (3)	0.0117 (3)	0.0079 (3)	0.000	0.000
Se4	0.0203 (3)	0.0203 (3)	0.0086 (4)	0.01016 (14)	0.000	0.000
Se5	0.0142 (2)	0.0142 (2)	0.0083 (4)	0.00712 (12)	0.000	0.000
In1	0.0345 (4)	0.0345 (4)	0.0431 (7)	0.0172 (2)	0.000	0.000
V1	0.0216 (16)	0.0095 (13)	0.0165 (16)	0.0038 (11)	0.000	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Mo2—Se5	2.5259 (8)	Mo3—Mo3 <sup>ii</sup>	2.7056 (10)
Mo2—Se2	2.5974 (6)	Mo3—Mo3 <sup>i</sup>	2.7056 (10)
Mo2—Se2 <sup>i</sup>	2.6290 (6)	Mo3—Mo2 <sup>ix</sup>	2.7136 (5)
Mo2—Mo2 <sup>i</sup>	2.6474 (7)	Mo3—Mo2 <sup>ii</sup>	2.7136 (5)
Mo2—Mo2 <sup>ii</sup>	2.6474 (7)	Mo3—Mo2 <sup>viii</sup>	2.7557 (5)
Mo2—Se1 <sup>iii</sup>	2.6504 (6)	In1—Se5	3.0759 (15)
Mo2—Se3 <sup>i</sup>	2.6966 (6)	In1—Se2 <sup>x</sup>	3.1221 (5)
Mo2—Mo3 <sup>i</sup>	2.7136 (5)	In1—Se2 <sup>xi</sup>	3.1221 (5)
Mo2—Mo3	2.7557 (5)	In1—Se2 <sup>iv</sup>	3.1221 (5)
Mo1—Se1 <sup>iv</sup>	2.5467 (7)	In1—Se1 <sup>x</sup>	3.4904 (7)
Mo1—Se4	2.5481 (8)	In1—Se1 <sup>xi</sup>	3.4904 (7)
Mo1—Se1	2.5717 (6)	In1—Se1 <sup>iv</sup>	3.4904 (7)
Mo1—Se1 <sup>v</sup>	2.6111 (6)	In1—Se3 <sup>vii</sup>	4.2444 (9)
Mo1—Se2	2.6378 (7)	In1—Se3 <sup>xii</sup>	4.2444 (9)
Mo1—Mo1 <sup>vi</sup>	2.6992 (7)	In1—Se3 <sup>xiii</sup>	4.2444 (9)
Mo1—Mo1 <sup>v</sup>	2.6992 (7)	V1—Se4	2.510 (2)
Mo1—Mo1 <sup>vii</sup>	2.7223 (8)	V1—Se4 <sup>viii</sup>	2.510 (2)
Mo1—Mo1 <sup>iv</sup>	2.7223 (8)	V1—Se3 <sup>v</sup>	2.730 (3)
Mo3—Se2	2.5631 (6)	V1—Se2 <sup>vi</sup>	2.7981 (18)
Mo3—Se2 <sup>viii</sup>	2.5631 (6)	V1—Se2 <sup>xiv</sup>	2.7981 (18)
Mo3—Se3	2.5965 (9)	V1—Se3 <sup>vi</sup>	2.831 (3)

Mo3—Se3 <sup>i</sup>	2.6095 (9)	V1—Mo3 <sup>vi</sup>	2.865 (3)
Se5—Mo2—Se2	92.603 (17)	Se2 <sup>viii</sup> —Mo3—Mo3 <sup>i</sup>	117.84 (2)
Se5—Mo2—Se2 <sup>i</sup>	91.858 (17)	Se3—Mo3—Mo3 <sup>i</sup>	118.92 (3)
Se2—Mo2—Se2 <sup>i</sup>	173.59 (3)	Se3 <sup>i</sup> —Mo3—Mo3 <sup>i</sup>	58.45 (3)
Se5—Mo2—Mo2 <sup>i</sup>	58.396 (13)	Mo3 <sup>ii</sup> —Mo3—Mo3 <sup>i</sup>	60.0
Se2—Mo2—Mo2 <sup>i</sup>	120.06 (2)	Se2—Mo3—Mo2 <sup>ix</sup>	149.88 (3)
Se2 <sup>i</sup> —Mo2—Mo2 <sup>i</sup>	58.978 (19)	Se2 <sup>viii</sup> —Mo3—Mo2 <sup>ix</sup>	59.685 (15)
Se5—Mo2—Mo2 <sup>ii</sup>	58.396 (13)	Se3—Mo3—Mo2 <sup>ix</sup>	60.991 (14)
Se2—Mo2—Mo2 <sup>ii</sup>	60.16 (2)	Se3 <sup>i</sup> —Mo3—Mo2 <sup>ix</sup>	118.165 (16)
Se2 <sup>i</sup> —Mo2—Mo2 <sup>ii</sup>	118.878 (19)	Mo3 <sup>ii</sup> —Mo3—Mo2 <sup>ix</sup>	61.129 (16)
Mo2 <sup>i</sup> —Mo2—Mo2 <sup>ii</sup>	60.0	Mo3 <sup>i</sup> —Mo3—Mo2 <sup>ix</sup>	89.824 (14)
Se5—Mo2—Se1 <sup>iii</sup>	90.42 (2)	Se2—Mo3—Mo2 <sup>ii</sup>	59.685 (15)
Se2—Mo2—Se1 <sup>iii</sup>	86.03 (2)	Se2 <sup>viii</sup> —Mo3—Mo2 <sup>ii</sup>	149.88 (3)
Se2 <sup>i</sup> —Mo2—Se1 <sup>iii</sup>	98.54 (2)	Se3—Mo3—Mo2 <sup>ii</sup>	60.991 (14)
Mo2 <sup>i</sup> —Mo2—Se1 <sup>iii</sup>	137.757 (18)	Se3 <sup>i</sup> —Mo3—Mo2 <sup>ii</sup>	118.165 (16)
Mo2 <sup>ii</sup> —Mo2—Se1 <sup>iii</sup>	129.74 (2)	Mo3 <sup>ii</sup> —Mo3—Mo2 <sup>ii</sup>	61.129 (16)
Se5—Mo2—Se3 <sup>i</sup>	175.68 (2)	Mo3 <sup>i</sup> —Mo3—Mo2 <sup>ii</sup>	89.824 (14)
Se2—Mo2—Se3 <sup>i</sup>	85.76 (2)	Mo2 <sup>ix</sup> —Mo3—Mo2 <sup>ii</sup>	112.47 (3)
Se2 <sup>i</sup> —Mo2—Se3 <sup>i</sup>	89.46 (2)	Se2—Mo3—Mo2 <sup>viii</sup>	145.46 (3)
Mo2 <sup>i</sup> —Mo2—Se3 <sup>i</sup>	119.150 (18)	Se2 <sup>viii</sup> —Mo3—Mo2 <sup>viii</sup>	58.328 (15)
Mo2 <sup>ii</sup> —Mo2—Se3 <sup>i</sup>	117.432 (18)	Se3—Mo3—Mo2 <sup>viii</sup>	118.823 (15)
Se1 <sup>iii</sup> —Mo2—Se3 <sup>i</sup>	93.45 (2)	Se3 <sup>i</sup> —Mo3—Mo2 <sup>viii</sup>	60.271 (14)
Se5—Mo2—Mo3 <sup>i</sup>	120.23 (2)	Mo3 <sup>ii</sup> —Mo3—Mo2 <sup>viii</sup>	88.941 (14)
Se2—Mo2—Mo3 <sup>i</sup>	116.35 (2)	Mo3 <sup>i</sup> —Mo3—Mo2 <sup>viii</sup>	59.578 (16)
Se2 <sup>i</sup> —Mo2—Mo3 <sup>i</sup>	57.311 (17)	Mo2 <sup>ix</sup> —Mo3—Mo2 <sup>viii</sup>	57.893 (17)
Mo2 <sup>i</sup> —Mo2—Mo3 <sup>i</sup>	61.851 (15)	Mo2 <sup>ii</sup> —Mo3—Mo2 <sup>viii</sup>	146.06 (3)
Mo2 <sup>ii</sup> —Mo2—Mo3 <sup>i</sup>	91.063 (14)	Se2—Mo3—Mo2	58.328 (15)
Se1 <sup>iii</sup> —Mo2—Mo3 <sup>i</sup>	138.90 (2)	Se2 <sup>viii</sup> —Mo3—Mo2	145.46 (3)
Se3 <sup>i</sup> —Mo2—Mo3 <sup>i</sup>	57.36 (2)	Se3—Mo3—Mo2	118.823 (15)
Se5—Mo2—Mo3	118.64 (2)	Se3 <sup>i</sup> —Mo3—Mo2	60.271 (14)
Se2—Mo2—Mo3	57.123 (17)	Mo3 <sup>ii</sup> —Mo3—Mo2	88.941 (14)
Se2 <sup>i</sup> —Mo2—Mo3	116.58 (2)	Mo3 <sup>i</sup> —Mo3—Mo2	59.578 (16)
Mo2 <sup>i</sup> —Mo2—Mo3	90.142 (14)	Mo2 <sup>ix</sup> —Mo3—Mo2	146.06 (3)
Mo2 <sup>ii</sup> —Mo2—Mo3	60.255 (15)	Mo2 <sup>ii</sup> —Mo3—Mo2	57.893 (17)
Se1 <sup>iii</sup> —Mo2—Mo3	131.66 (2)	Mo2 <sup>viii</sup> —Mo3—Mo2	109.90 (3)
Se3 <sup>i</sup> —Mo2—Mo3	57.177 (19)	Mo1 <sup>vii</sup> —Se1—Mo1	64.26 (2)
Mo3 <sup>i</sup> —Mo2—Mo3	59.29 (2)	Mo1 <sup>vii</sup> —Se1—Mo1 <sup>vi</sup>	63.70 (2)
Se1 <sup>iv</sup> —Mo1—Se4	176.34 (2)	Mo1—Se1—Mo1 <sup>vi</sup>	62.77 (2)
Se1 <sup>iv</sup> —Mo1—Se1	88.948 (17)	Mo1 <sup>vii</sup> —Se1—Mo2 <sup>xv</sup>	131.23 (2)
Se4—Mo1—Se1	91.765 (17)	Mo1—Se1—Mo2 <sup>xv</sup>	128.19 (2)



## supplementary materials

---

Se1 <sup>iv</sup> —Mo1—Se1 <sup>v</sup>	88.084 (17)	Mo1 <sup>vi</sup> —Se1—Mo2 <sup>xv</sup>	81.114 (19)
Se4—Mo1—Se1 <sup>v</sup>	90.859 (17)	Mo3—Se2—Mo2	64.549 (18)
Se1—Mo1—Se1 <sup>v</sup>	173.79 (3)	Mo3—Se2—Mo2 <sup>ii</sup>	63.004 (18)
Se1 <sup>iv</sup> —Mo1—Se2	93.50 (2)	Mo2—Se2—Mo2 <sup>ii</sup>	60.86 (2)
Se4—Mo1—Se2	90.13 (2)	Mo3—Se2—Mo1	130.39 (2)
Se1—Mo1—Se2	86.306 (19)	Mo2—Se2—Mo1	126.33 (2)
Se1 <sup>v</sup> —Mo1—Se2	99.32 (2)	Mo2 <sup>ii</sup> —Se2—Mo1	81.018 (19)
Se1 <sup>iv</sup> —Mo1—Mo1 <sup>vi</sup>	119.568 (17)	Mo3—Se3—Mo3 <sup>ii</sup>	62.62 (3)
Se4—Mo1—Mo1 <sup>vi</sup>	58.018 (12)	Mo3—Se3—Mo2 <sup>ix</sup>	61.649 (16)
Se1—Mo1—Mo1 <sup>vi</sup>	59.33 (2)	Mo3 <sup>ii</sup> —Se3—Mo2 <sup>ix</sup>	62.551 (16)
Se1 <sup>v</sup> —Mo1—Mo1 <sup>vi</sup>	117.827 (19)	Mo3—Se3—Mo2 <sup>ii</sup>	61.649 (16)
Se2—Mo1—Mo1 <sup>vi</sup>	129.11 (2)	Mo3 <sup>ii</sup> —Se3—Mo2 <sup>ii</sup>	62.551 (16)
Se1 <sup>iv</sup> —Mo1—Mo1 <sup>v</sup>	118.595 (17)	Mo2 <sup>ix</sup> —Se3—Mo2 <sup>ii</sup>	113.56 (3)
Se4—Mo1—Mo1 <sup>v</sup>	58.018 (12)	Mo1 <sup>vi</sup> —Se4—Mo1	63.96 (2)
Se1—Mo1—Mo1 <sup>v</sup>	119.25 (2)	Mo1 <sup>vi</sup> —Se4—Mo1 <sup>v</sup>	63.96 (2)
Se1 <sup>v</sup> —Mo1—Mo1 <sup>v</sup>	57.903 (19)	Mo1—Se4—Mo1 <sup>v</sup>	63.96 (2)
Se2—Mo1—Mo1 <sup>v</sup>	137.270 (18)	Mo2 <sup>i</sup> —Se5—Mo2	63.21 (3)
Mo1 <sup>vi</sup> —Mo1—Mo1 <sup>v</sup>	60.0	Mo2 <sup>i</sup> —Se5—Mo2 <sup>ii</sup>	63.21 (3)
Se1 <sup>iv</sup> —Mo1—Mo1 <sup>vii</sup>	59.30 (2)	Mo2—Se5—Mo2 <sup>ii</sup>	63.21 (3)
Se4—Mo1—Mo1 <sup>vii</sup>	118.273 (15)	Mo2 <sup>i</sup> —Se5—In1	142.763 (16)
Se1—Mo1—Mo1 <sup>vii</sup>	57.423 (15)	Mo2—Se5—In1	142.763 (16)
Se1 <sup>v</sup> —Mo1—Mo1 <sup>vii</sup>	116.42 (2)	Mo2 <sup>ii</sup> —Se5—In1	142.763 (16)
Se2—Mo1—Mo1 <sup>vii</sup>	132.182 (19)	Se4 <sup>viii</sup> —V1—Se4	84.98 (9)
Mo1 <sup>vi</sup> —Mo1—Mo1 <sup>vii</sup>	60.281 (10)	Se4 <sup>viii</sup> —V1—Se3 <sup>v</sup>	87.27 (7)
Mo1 <sup>v</sup> —Mo1—Mo1 <sup>vii</sup>	90.0	Se4—V1—Se3 <sup>v</sup>	87.27 (7)
Se1 <sup>iv</sup> —Mo1—Mo1 <sup>iv</sup>	58.31 (2)	Se4 <sup>viii</sup> —V1—Se2 <sup>vi</sup>	166.76 (13)
Se4—Mo1—Mo1 <sup>iv</sup>	118.273 (15)	Se4—V1—Se2 <sup>vi</sup>	87.36 (2)
Se1—Mo1—Mo1 <sup>iv</sup>	116.86 (2)	Se3 <sup>v</sup> —V1—Se2 <sup>vi</sup>	103.16 (8)
Se1 <sup>v</sup> —Mo1—Mo1 <sup>iv</sup>	56.998 (14)	Se4 <sup>viii</sup> —V1—Se2 <sup>xiv</sup>	87.36 (2)
Se2—Mo1—Mo1 <sup>iv</sup>	140.74 (2)	Se4—V1—Se2 <sup>xiv</sup>	166.76 (13)
Mo1 <sup>vi</sup> —Mo1—Mo1 <sup>iv</sup>	90.0	Se3 <sup>v</sup> —V1—Se2 <sup>xiv</sup>	103.16 (8)
Mo1 <sup>v</sup> —Mo1—Mo1 <sup>iv</sup>	60.281 (10)	Se2 <sup>vi</sup> —V1—Se2 <sup>xiv</sup>	97.98 (8)
Mo1 <sup>vii</sup> —Mo1—Mo1 <sup>iv</sup>	59.44 (2)	Se4 <sup>viii</sup> —V1—Se3 <sup>vi</sup>	85.09 (8)
Se2—Mo3—Se2 <sup>viii</sup>	110.93 (3)	Se4—V1—Se3 <sup>vi</sup>	85.09 (8)
Se2—Mo3—Se3	93.18 (2)	Se3 <sup>v</sup> —V1—Se3 <sup>vi</sup>	169.63 (12)
Se2 <sup>viii</sup> —Mo3—Se3	93.18 (2)	Se2 <sup>vi</sup> —V1—Se3 <sup>vi</sup>	83.50 (6)
Se2—Mo3—Se3 <sup>i</sup>	88.30 (2)	Se2 <sup>xiv</sup> —V1—Se3 <sup>vi</sup>	83.50 (6)
Se2 <sup>viii</sup> —Mo3—Se3 <sup>i</sup>	88.30 (2)	Se4 <sup>viii</sup> —V1—Mo3 <sup>vi</sup>	122.97 (8)
Se3—Mo3—Se3 <sup>i</sup>	177.38 (3)	Se4—V1—Mo3 <sup>vi</sup>	122.97 (8)
Se2—Mo3—Mo3 <sup>ii</sup>	120.789 (19)	Se3 <sup>v</sup> —V1—Mo3 <sup>vi</sup>	136.14 (12)
Se2 <sup>viii</sup> —Mo3—Mo3 <sup>ii</sup>	120.789 (19)	Se2 <sup>vi</sup> —V1—Mo3 <sup>vi</sup>	53.80 (4)

Se3—Mo3—Mo3 <sup>ii</sup>	58.92 (3)	Se2 <sup>xiv</sup> —V1—Mo3 <sup>vi</sup>	53.80 (4)
Se3 <sup>i</sup> —Mo3—Mo3 <sup>ii</sup>	118.45 (3)	Se3 <sup>vi</sup> —V1—Mo3 <sup>vi</sup>	54.23 (5)
Se2—Mo3—Mo3 <sup>i</sup>	117.84 (2)		

Symmetry codes: (i)  $-y+1, x-y, z$ ; (ii)  $-x+y+1, -x+1, z$ ; (iii)  $-x+y+1, -x, z$ ; (iv)  $x-y, x, -z+1$ ; (v)  $-y, x-y, z$ ; (vi)  $-x+y, -x, z$ ; (vii)  $y, -x+y, -z+1$ ; (viii)  $x, y, -z+3/2$ ; (ix)  $-x+y+1, -x+1, -z+3/2$ ; (x)  $-x+1, -y, -z+1$ ; (xi)  $y+1, -x+y+1, -z+1$ ; (xii)  $x-y+1, x, -z+1$ ; (xiii)  $-x+1, -y+1, -z+1$ ; (xiv)  $-x+y, -x, -z+3/2$ ; (xv)  $-y, x-y-1, z$ .

Fig. 1

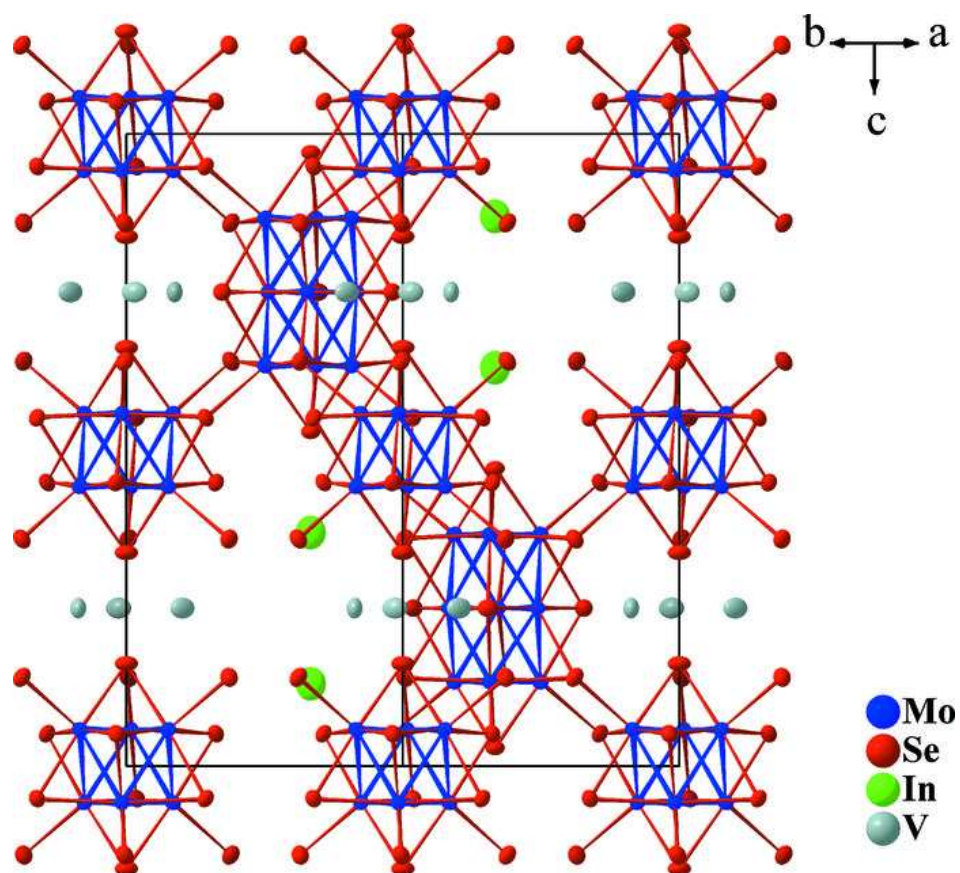


Fig. 2

